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13. ABSTRACT *(Maximum 200 words)*

This research program is centered on exploring and studying the fundamental mechanisms underlying novel nonlinear optical properties of liquid crystals in their isotropic as well as liquid crystalline phases. Experimental and theoretical studies involving nonlinear optical wave mixing, short pulse propagation in nonlinear fiber core, and polarization selective holography were conducted. The technical achievements obtained may be summarized in the following two broad categories.:- (i) Development of an extremely nonlinear fiber core liquid characterized by an intensity-dependent effective two-photon absorption coefficient that ranks among the largest of all known nonlinear liquids. In particular, the liquid cored fiber is capable of high (linear) transmission, and limits picosecond - nanosecond laser pulses to below sensor/eye damage level. Detailed model for describing the nonlinear photonic processes and molecular dynamics of the fiber core liquid have also been developed. (ii) Discovery of two nematic liquid crystalline materials that exhibit supra-optical nonlinearities, methyl-red and azobenzene-LC doped nematic liquid crystals (NLC). The nonlinear index change coefficients of these NLC are found to be in the range of 2 – 20 cm^2/W. These nonlinear films enable feasibility demonstration of some advanced all-optical operations such as optical limiting and anti-glare operation against long pulse or cw lasers at submicrowatt power, incoherent-coherent image conversion and image inversion, dynamic and storage holographic grating formation.

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1. Statement of the Problems Studied.

This research program is centered on exploring and studying the fundamental mechanisms underlying novel nonlinear optical properties of liquid crystals in their isotropic as well as liquid crystalline phases. Experimental and theoretical studies involving nonlinear optical wave mixing, short pulse propagation in nonlinear fiber core, and polarization selective holography were conducted. The technical achievements obtained may be summarized in the following two broad categories.:- (i) Development of an extremely nonlinear fiber core liquid characterized by an intensity-dependent effective two-photon absorption coefficient that ranks among the largest of all known nonlinear liquids. In particular, the liquid cored fiber is capable of high (linear) transmission, and limits picosecond - nanosecond laser pulses to below sensor/eye damage level. Detailed model for describing the nonlinear photonic processes and molecular dynamics of the fiber core liquid have also been developed. (ii) Discovery of two nematic liquid crystalline materials that exhibit supra-optical nonlinearities, methyl-red and azobenzene-LC doped nematic liquid crystals (NLC). The nonlinear index change coefficients of these NLC are found to be in the range of $2 - 20\ cm^2/W$. These nonlinear films enable feasibility demonstration of some advanced all-optical operations such as optical limiting and anti-glare operation against long pulse or cw lasers at submicrowatt power, incoherent-coherent image conversion and image inversion, dynamic and storage holographic grating formation.

2. Scientific Progress and Accomplishment

2.1 Nonlinear Fiber Structures and Optical Limiting of Short Laser Pulses

Liquid crystals are complex organic molecular systems that exhibit various mesophases characterized by the degree of order. In isotropic liquid crystals, optical and nonlinear optical properties are governed by individual molecular response. Individual electronic nonlinear optical responses of liquid crystals are among the largest of all known materials. These fast nonlinearities, and the relatively much smaller scattering loss make isotropic liquid crystals ideal candidates for processes involving long interaction length and short laser pulses, such as those nonlinear absorption processes occurring in the guiding cores of fiber arrays intended for optical limiting application.

In the course of this research program which involved various nonlinear optical studies of a large number of isotropic liquid crystals, we have identified an extremely nonlinear fiber core liquid, the so-called L34 that is characterized by an intensity-dependent effective two-photon absorption coefficient that ranks among the largest of all known nonlinear liquids. Furthermore, we have also formulated the chemical pathway that enable us to synthesze sizeable quantity of this liquid for practical device fabrication. One of the major achievements made in this program is the demonstration of a practical optical limiting device that could protect eye and optical sensors from agile frequency laser pulses.

An important requirement for optical limiting of short laser pulses is that the device/material should limit the transmitted laser energy to less than 1 μJ [above which damage to the retina, for example, is likely]. In fiber array where the constituent

isotropic liquid crystal cored fiber is 5 mm long, and the core diameter is 20 μm, for example, the required nonlinear absorption coefficient β_{eff} is > 0.6 cm/GW for picosecond laser pulses. On the other hand, for nanosecond laser pulses, the required β_{eff} value should be > 91 cm/GW. In this context, the isotropic liquid crystals L34 synthesized in our laboratory is particularly noteworthy, as it possesses effective nonlinear absorption coefficients β_{eff} larger than the required values mentioned above, and gives perhaps the best optical limiting performance among all the materials under active investigation.

L34 possesses an effective nonlinear absorption coefficient $\beta_{eff} \sim 300$ cm/GW for nanosecond laser pulses, and an effective nonlinear absorption $\beta_{eff} \sim 10$ cm/GW for picosecond laser pulses. These values of effective nonlinear coefficients obtained by optical limiting measurements in L34 cored fibers are also in good agreement with two separate z-scan absorption studies of bulk L34 films - one conducted at the Army Research Laboratory, Adelphi, Maryland, and one at CREOL- University of Central Florida. L34 also possesses good transparency in the entire visible spectrum.

As a result of these unusually large nonlinear absorption properties of the fiber core liquids, the fiber arrays fabricated using these liquids exhibit exceptional optical limiting capabilities against nanosecond-picosecond laser pulses. Tables I below summarize some of the optical limiting performance characteristics obtained in our laboratory.

Table I. Nonlinear Liquid Cored Fiber Arrays – nanosecond laser pulses

Core:	Doped ILC [ILC: Isotropic liquid crystal]	Doped ILC	L34
Cladding:	Transparent	Opaque	Opaque
Limiting Mechanisms			
Nonlinear scattering, Nonlinear absorption , Reverse saturable absorption Excited state absorption - core			
Limiting Threshold			
	0.5 μJ	0.1 μJ	0.1 μJ
Clamped Transmission			
(energy)	~ 1 μJ	0.6 μJ	0.4 μJ
	[0.1 μJ is equivalent to a fluence of 0.01 J/cm^2 with 10^5 gain]		
Dynamic Range [Pin-Prick damage spot - insignificant loss of viewing]			
	560	>1000	>1000
Spectral Operation Range			
	532 nm (Demonstrated)	400 nm -700 nm (anticipated)	
Damage Phenomena: pin-prick blemishes at ~ 200 μJ [not detrimental to field of view]			

As pointed before[1,2], one great advantage of using such fiber array with liquid core is that for higher incident laser energies, the transmission will drop even further because of bubble formation and/or other high order nonlinear optical effects occurring at the fiber entrance plane or within the core. Therefore, the dynamic range of the fiber array limiter can be >>1000.

2.2 Molecular Photonics – Characterization and Modeling

We have also developed the theoretical model for various photonic absorption processes in L34. Fig 1 shows the energy level scheme involved in the molecular photonics processes.

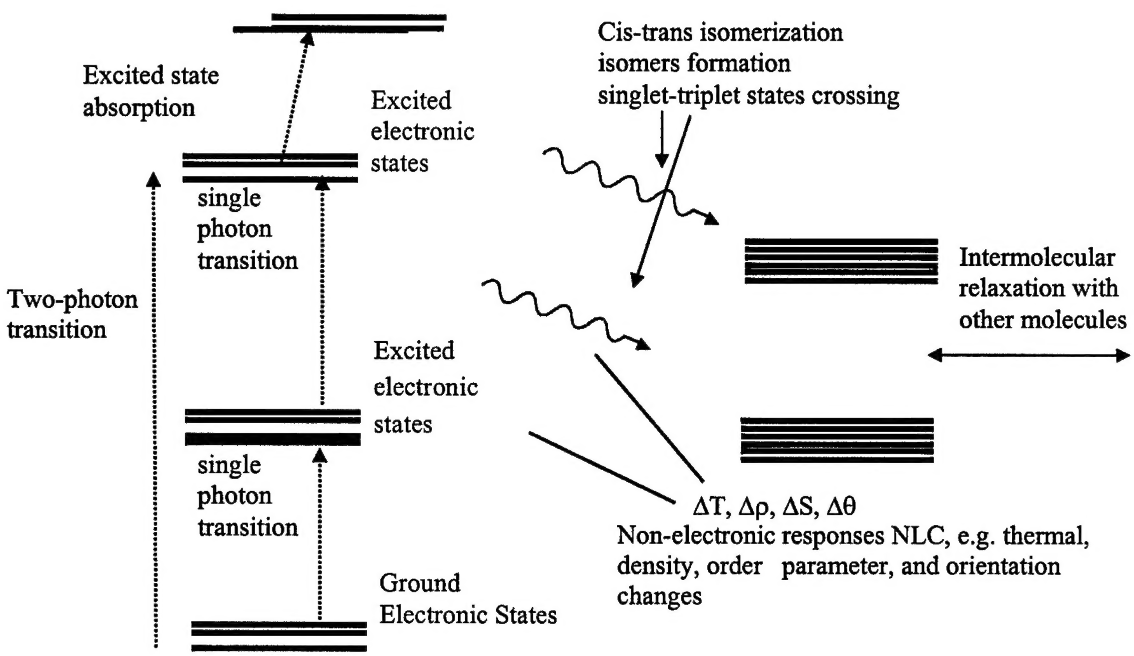

Fig.1. Electronic and non-electronic nonlinear optical processes occurring in the fiber core liquid.

The ground state is very weakly connected to the intermediate electronic level [since L34 is transparent in the visible spectrum], but is strongly connected to the two-photon state, from which it can undergo excited state absorption and/or intersystem crossings.

For nonlinear optical pulse propagation and absorption in fiber core formed with this liquid, it is also necessary to formulate the appropriate equations. In particular, the nonlinear absorption/propagation can be described by the following equation

$$\frac{dI}{dz} = -\alpha_g\left(\frac{N_1}{N_0}\right)I - \alpha_i\left(\frac{N_i}{N_0}\right)I - \alpha_{exc}\left(\frac{N_2}{N_0}\right)I - \beta\left(\frac{N_1}{N_0}\right)I^2 \qquad (1)$$

and a set of dynamical equations for the level population densities Ni (i = 1, 2, 3,...etc.).

To solve these equations in quantitive manners, various molecular optical parameters of L34 have to be characterized. For these purposes, we have employed picosecond and nanosecond pump-probe dynamical transmission studies as well as z-acan techniques. For the latter studies, collaborations with the Army Research Laboratory [Mary Miller] and the University of Central florida (CREOL) have yielded valuable and consistent data on the effective nonlinear absorption coefficients as quoted in the preceding section of this report. Fig. 2 a-d shows the typical z-scans obtained and a typical output/input limiting curve of the nonlinear fiber. Detailed analysis of these fundamental material characterization studies and fiber limiting performance are given in the publications as listed in section 3.

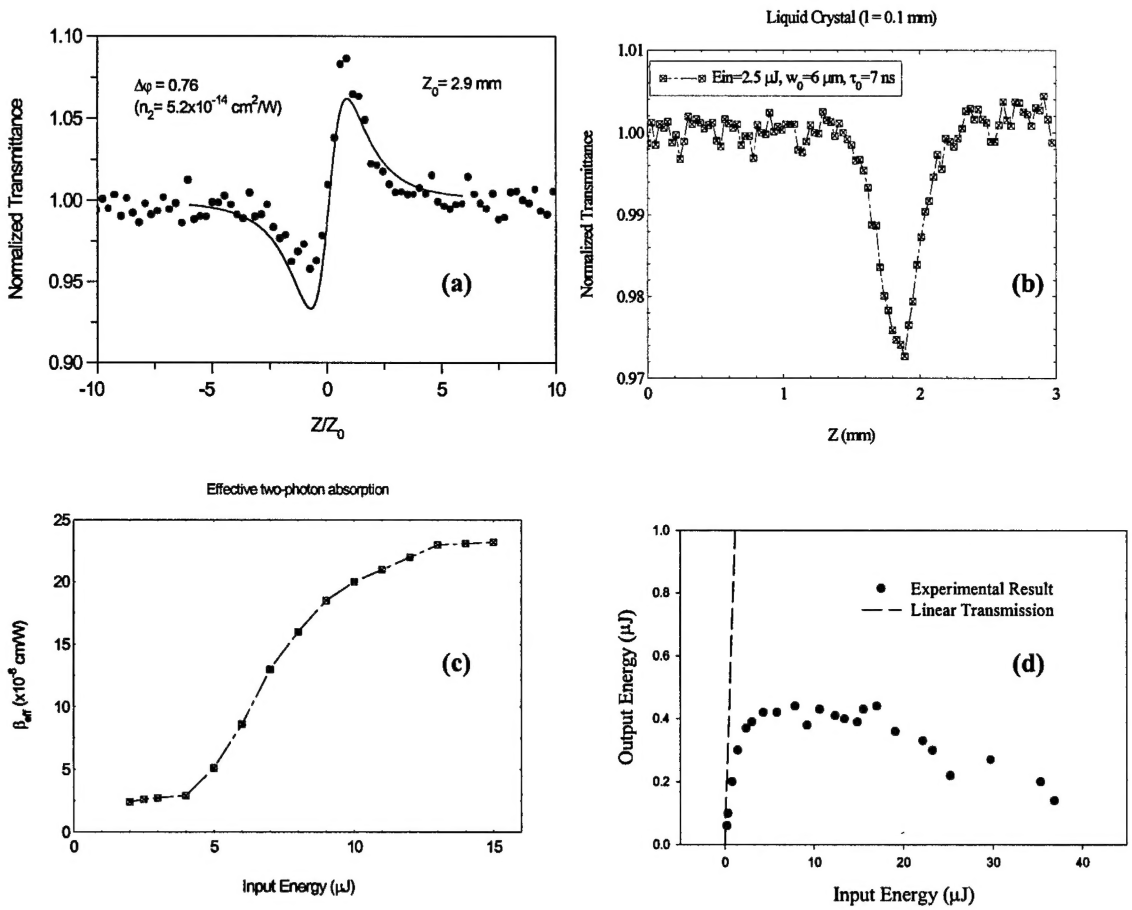

Fig. 2 (a) Picosecond and (b) nanosecond z-scan of the bulk L34 liquid. In (a), the laser pulsewidth τ_p = 15 ps, focused laser beam waist ω_o = 22 μm. In (b), τ_p = 7 ns and ω_o = 6 μm. (c) Plot of the $\beta_{eff}(I)$ (in unit of 10^{-8} cm/GW) as a function of the input laser pulse energy for a 100 μm thick bulk L34 film. (d) Output vs. input plot of 20 nanoseconds laser pulse through a 3 mm long constituent fiber of an opaque-cladding fiber array.

2.3. Discovery of Extremely Nonlinear Optical Responses in the Nematic Liquid Crystalline Phase.

Nonlinear absorption processes become ineffective at longer time scale, since the power of the laser for a given energy scales inversely as the the pulse duration. For the microseconds – cw time scale, we have to turn to other alternatives such as the recently discovered supra-nonlinear methyl-red doped nematic liquid crystal (MRNLC) films and azobenzene liquid crystal doped NLC (AZONLC). In both MRNLC and AZONLC films, the refractive index change is due to laser induced reorientation of the birefringent director (crystalline) axis of the nematic liquid crystal host. Typical birefringence of NLC is about 0.2 ($n_e \sim 1.7$ and $n_o \sim 1.5$). **Fig. 3** depicts the various processes that could occur in these NLC systems that could cause director axis reorientation. In the case of MRNLC, the underlying processes are closely related to the photo-charge producing properties of the dopant - reminiscent of photorefractive effects. On the other hand, AZONLC, an unusually efficient form of photo-induced trans-cis isomerization process is believed to be at work, which results in a very large order parameter and refractive index changes.

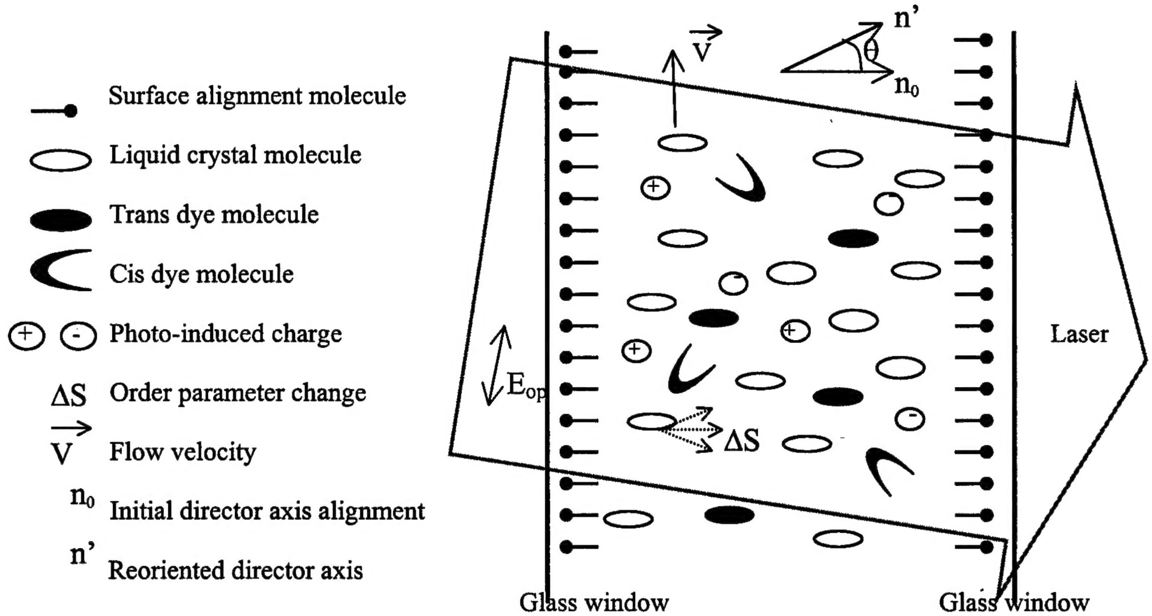

Fig. 3. Schematic depiction of various laser-induced photochemical and photo-physical processes in a nematic liquid crystal film.

The nonlinear refractive index coefficient of these liquid crystalline materials and other materials are listed in Table 1. In terms of the nonlinear index coefficient n_2, MRNLC and BMAB doped NLC are arguably the most nonlinear optical materials known to date. Such large nonlinearities allow us to demonstrate several image processing and optical limiting effects with extremely low threshold power/intensity. In particular, we recently showed that with an MRNLC film and crossed polarizers, one can construct an anti-laser-jamming device capable of removing the bright dazzling laser spot from the field of view, and a dynamic range exceeding 3000. These nematic

films could be integrated with the fiber array to construct extremely broad temporal range eye/sensor protection device over the entire visible spectrum.

Table II. Refractive Index Coefficients of Nonlinear Optical Materials

Materials	Order of Magnitude of n_2 (cm^2/W)
Nematic Liquid Crystal	
Purely optically induced[ref.1] or thermal effect	10^{-4}
Excited dopant assisted[ref. 21]	10^{-3}
Photorefractive -C60 doped [ref.10]	10^{-3}
Photorefractive -methyl-red doped[ref. 3,4]	**10**
BMAB doped NLC [ref. 7]	**>2**
Cis-trans isomery [ref. 20]	10^{-3}
GaAs bulk [ref.24]	10^{-5}
GaAs MQW [ref. 25]	10^{-3}
Photorefractive crystals and polymers[26]	10^{-4}
Bacteriorhodopsin [ref.27]	10^{-3}
Organic Polymers[ref. 28]	10^{-13}

In conclusion, a new class of isotropic liquid crystal has been discovered. Picosecond and nanosecond pulsed laser studies have revealed that the liquid possesses an unique excited-state enhanced two- and multi-photon absorption pathway, leading to by far the largest known effective nonlinear coefficient suitable for optical limiting application in conjunction with the patented nonlinear fiber array concept. An extremely nonlinear dye-doped nematic liquid crystal material has also been discovered. These materials contain photo-charge producing agents, and will undergo laser induced director axis reorientation and order parameter changes to give rise to a refractive index change coefficient that is orders of magnitude larger than all known nonlinear optical materials.

Both discoveries invite envision of new high performance optical devices, and open up many interesting and important fundamental questions on the individual and collective molecular nonlinear optical responses of these complex liquid crystalline materials. Recently this research group was granted a DURIP equipment award by the Army Research Office, and a renewal of the main research program. Using the broad temporal and spectral characteristics of the new laser system, plans are underway to conduct a variety of nonlinear optical experiments including pump-probe spectroscopy, dynamic and storage gratings, two- and multi- photon absorption spectroscopy, z-scans measurements and excited state absorption spectroscopy. The goals are to address many interesting and important questions on the basic mechanisms occurring in these newly developed classes of ultra-nonlinear optical material systems. In particular, the exact mechanism(s) underlying these large nonlinearities, fundamental time constants involved in various inter- and intra- molecular relaxations, trans-cis isomerization and order parameter changes, and multi-photonic absorptions embedded in the vast temporal and spectral regimes still await quantitative exploration. A well-concerted study will be valuable not only to further our understanding of these novel ultra-nonlinear optical materials, but also to provide insights into new material synthesis and establish the

applicability of the observed effects in spectral and temporal regime not accessible by other materials.

3. List of Papers Published

1. I. C. Khoo, M. V. Wood, B. D.Guenther, Min-Yi Shih and P. H. Chen, " Nonlinear- absorption and optical limiting of laser pulses in a liquid-cored fiber array," J. Opt. Soc. Am. B15, pp. 1533-1540, 1998.

2. I .C. Khoo, S. Slussarenko, B. D. Guenther and W. V. Wood, "Optically Induced Space Charge Fields, DC Voltage, and Extraordinarily Large Nonlinearity in Dye-doped Nematic Liquid Crystals," Opt. Letts 23, pp 253 - 255 (1998).

3. I. C. Khoo, M. V. Wood, B. D. Guenther, Min-Yi Shih, P. H. Chen, Zhaogen Chen and Xumu Zhang, "Liquid Crystal Film and Nonlinear Optical Liquid Cored Fiber Array for ps-cw Frequency Agile Laser Optical Limiting Application". Optics Express, Vol. 2, no. 12.pp 471-82, (1998)

4. I. C. Khoo, M.V. Wood, P. Chen , Min-Yi Shih and Brett. D. Guenther. "Self-defocusing and Optical Limiting of NanoWatt cw Laser and Image Processing at μWatt/cm2 intensity with nematic liquid crystals". SPIE Int. Symp. on Optical Science, Engineering and Instrumentation, San Diego, 1998. Proceeding Vol. 3475 .

5. I. C. Khoo, P. H. Chen, M.V. Wood, M.Y. Shih, "Nanosecond and picosecond studies of an extremely nonlinear fiber core liquid for limiting application," SPIE's Int. Symp. on Optical Science, Engineering and Instrumentation, Denver, 1999. Proceeding Vol. 3798.

6. I. C. Khoo " Nonlinear Optical Properties of Nmeatic Liquid Crystals", *in Physical Properties of Liquid Crystals* Ed. D. A. Dunmur, A. Fukuda and G. R. Luckhurst (INSPEC, IEE, London, UK, 1999)

7. I. C. Khoo, M. Y. shih, P. H. Chen, M. V. Wood, "Photosensitive liquid crystals for dynamic holography and electro-optics," SPIE Int. Symp. on Optical Science, Engineering and Instrumentation, Denver, 1999. Proceeding Vol. 3800.

8. I. C. Khoo, M. V. Wood, M. Y. Shih and P. H. Chen, "Extremely Nonlinear Photosensitive Liquid Crystals for Image Sensing and Sensor Protection," Optics Express, Vol. 4, no. 11, pp 431-442 (1999) [Electronics Journal]

9. I. C. Khoo, P. H. Chen, M. V. Wood, and Min-Yi Shih, " Molecular photonics of a highly nonlinear organic fiber core liquid for picosecond -nanosecond optical limiting effect", Chemical Physics Vol. 245, pp. 517-531(1999).

10. I. C. Khoo, Min-Yi Shih, M. V. Wood, B. D. Guenther, and P. H. Chen, F. Simoni, S. Slussarenko*, O. Francescangeli, L. Lucchetti"Dye-doped photorefractive liquid crystals for dynamic and storage holographic grating formation and spatial light modulation," IEEE Proceedings Vol. 87, no. 11, pp 1897 – 1911 (1999)

11. I. C. Khoo' "Nonlinear fiber core liquid and nematic liquid crystal film for wide temporal bandwidth optical limiting application," *in Thin Films for Optical Waveguide Devices and Materials for Optical Limiting*, ed. K. Nashimoto, et al – Proceedings of Material Research Society Meeting, Boston 12/1999.

12. I. C. Khoo, P. H. Chen, M. Y. Shih, A. Shishido, S. Slussarenko and M. V. Wood, "Supra Optical Nonlinearities of Methyl-Red and Azobenzene Liquid Crystal –doped Nematic Liquid Crystals," Molecular Crystals Liquid Crystals.[In Press, 2000]

4. Invited Conference Presentations

*1. Photorefractivity, Optical Wave Mixing and Holographic Grating Formation in Nematic Liquid Crystals. I. C. Khoo. Invited Paper -International Topical Meeting on Optics of Liquid Crystals, Heppenheim, Germany 9/1997.

*2. Extremely sensitive photorefractive liquid crystals for dynamic holography and optical storage applications. I. C. Khoo. Invited Plenary Paper. Int. Symp. on Image Processing Molecular Systems IPMS '98, Tsukuba, Japan. March 9-10,1998

*3. Nonlinear Optical Liquid Cored Fiber Array and Liquid Crystalline Films for Optical Sensor Protection Application . I. C. Khoo. US/UK Optical Limiter Modeling Workshop, Air Force Research Laboratory - Materials and manufacturing Directorate, Wright Patterson AFB, OH. 18-21 May 1998

*4. Nonlinear optical liquid cored fiber array and liquid crystalline film for optical limiting of frequency agile picosecond pulsed - cw lasers. I. C. Khoo. Invited plenary paper. First Int. Workshop on Optical Power Limiting. Cannes, France, June 29 -July 1, 1998.

*5. Novel liquid-cored fiber and liquid crystal film for sensor protection against visible ps-cw lasers. I. C. Khoo. Invited paper. SPIE's Int. Symp. on Optical Science, Engineering and Instrumentation. San Diego 7/20 -7/24, 1998.

*6. Self-defocusing and Optical Limiting of NanoWatt cw Laser and Image Processing at μWatt/cm2 intensity with nematic liquid crystals. I. C. Khoo. Invited Paper. SPIE's Int. Symp. on Optical Science, Engineering and Instrumentation. San Diego 7/20 -7/24, 1998.

*7. Extremely nonlinear dye-doped nematic liquid crystal for next-generation wave mixing and sensing application. I.C. Khoo, B. D. Guenther, Min -Yi Shih, P. Chen and W. V. Wood. Annual Meeting of the Optical Society of America, Oct. 5, 1998. Baltimore.

*8. Nematic liquid crystal film with a nonlinear index coefficient of over 10 cm2/Watt and ms response speed. I. C. Khoo, Min -Yi Shih, P. H. Chen , M. V.

Wood and B. D. Guenther. Annual Meeting of IEEE Lasers and Electro-Optics Society, Dec. 1 -4, 1998.
*9. I. C. Khoo, "Extremely nonlinear photosensitive liquid crystals", Invited Paper, *European Material Research Conference*, Strasbourg, France, 6/1999.

*10.I. C. Khoo, "Supra Optical Nonlinearities of Methyl-Red and Azobenzene Liquid Crystal –doped Nematic Liquid Crystals," Invited paper 8th International Topical Meeting on 'Optics of Liquid Crystals', Puerto Rico, USA 9/99.

*11. I. C. Khoo, "Extremely nonlinear photosensitive liquid crystalline materials" Invited Paper, Chitose International Forum on Photonic Sciences, Chitose City, Hokkaido, Japan, Oct. 1999.

*12. I. C. Khoo' "Nonlinear fiber core liquid and nematic liquid crystal film for wide temporal bandwidth optical limiting application," Invited Paper, *Materials for Optical Limiting*, Material Research Society Meeting, Boston 12/1999.

*13. I. C. Khoo. "Liquid Crystal Photorefractivity – Towards Supra-Optical Nonlinearity,". Invited Paper. European Material Research Symposium, Strasbourg, France, 5/2000.

*14. I. C. Khoo, "Modeling Nonlinear Photonics of Nonlinear Fiber Core for Optical Limiting Application" Invited Paper. SPIE SPIE's Int. Symp. on Optical Science, Engineering and Instrumentation, San Diego, 8/2000.

5. Report of Inventions

An invention disclosure entitled " Methyl-red doped nematic liquid crystal for dynamic holography, spatial light modulation and optical limiting" – PSU Invention Disclosure # 98-1919, is filed by the principal investigator with Pennsylvania State University Intellectual Property Office on April 15, 1998.

6. Participating Scientific Personnel

The personnel involed in this project includes the principal investigator, Prof. I. C. Khoo, three senior Ph. D. graduate students- Michael Wood, Min-Yi Shih and P. H. Chen. Michael Wood is supported by a DOD ASSERT Fellowship.